Programmable Self-Aligning Liquid Magnetic Nanoparticle Masks and Methods for Their Use

Introduction

5   This patent application claims the benefit of priority from U.S. Provisional Patent Application Serial No. 60/533,274, filed December 30, 2003, which is hereby incorporated by reference in its entirety.

Field of the Invention

15   The present invention relates to magnetic nanoparticle masks and methods for their use. The masking materials are not only compatible with traditional photolithographic processes but can also be used to assist in the fabrication of emerging medical, optical and wireless devices. In this
20   method, a suspension of magnetic nanoparticles such as ferrofluid, which is composed of ultra-fine iron oxide grains, is used to protect and/or deprotect selected areas of a magnetically programmable substrate. Automatic mask formation and registration is controlled by magnetic field
25   gradients produced either remotely or produced by materials contained on the substrate. Application of external magnetic fields to the system causes the magnetic nanoparticles to aggregate only at regions of magnetic field maxima, thereby masking those areas from, for example,
30   ultraviolet radiation, chemical or physical etchants, ion implantation, chemical exposure, or binding of a molecule such as a protein or nucleic acid. This method is particularly useful in the fabrication of patterned

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substrates used, for example in combinatorial chemistry,
drug discovery and genomics, wherein features of the
substrate are micron- or submicron-sized. Applications of
magnetic particle masks also exist in the fabrication of
5   optically or electrically conductive interconnects for use
in arranging electronic and optical systems. Magnetic
nanoparticle masks also find use in arranging diverse
materials or components onto flexible, curved and/or plastic
substrates. These abilities are expected to be useful in
10   the fabrication of biomedical implants and Radio Frequency
Identification (RFID) tags.

Background of the Invention
Multi-component surfaces are of enormous importance
15   with applications in electronics, photonics, genome
analysis, drug discovery, and cellular systems. Surfaces
designed with a precise arrangement of conductive or
insulating materials form the basis of modern electronic
devices. Chemically heterogeneous surfaces have been
20   fabricated for use in biochemical sensing (Fodor et al.
Nature 1993 364:555) and in assembling arrays of living
cells (Graighead et al. Curro Opin. Solid State Mat. Sci.
2001 5:177). In general, previous strategies for
fabricating such devices have relied on highly planar
25   surfaces formed from brittle crystalline materials, such as
silicon or gallium arsenide. These fabrication strategies
often employ high temperatures, pressure, chemical solvents
and other harsh conditions, which cannot be used on more
delicate materials. Today, there is an emerging paradigm of
30   microdevices based on surfaces that are highly curved or
flexible, and on materials that are soft or delicate, such
as organic molecules and other polymers. There is a need
for new patterning strategies that can handle these

materials and surfaces. Several groups have attempted to
fabricate these surfaces by direct writing methods using
converted scanning probe microscopes (Demers et al. Science
2002 295:1701; Cao et al. Science 2002 296:1838; and
5   Bruckbauer et al. JACS 2003 125:9834); however these methods
are only useful for patterning small areas. Other techniques
have been based on self-assembly (or bottom-up assembly).
Self-assembly techniques are massively parallel; however,
most traditional self-assembly techniques fall short when it
10   comes to assembling more than one type of component.
Accordingly, building multi-component surfaces on a
commercial scale at the nanoscale and microscale level has
remained a major challenge because of the high precision and
parallelism that is simultaneously required to create such
15   surfaces. While significant time and resources have been
invested in the area of multi-component nanopatterning, no
single technique has been developed to date that is capable
of satisfying both requirements of resolution and speed.

     Fabrication of heterogeneous substrates of the kind
20   used for combinatorial chemistry, drug discovery and
genomics typically requires multiple lithographic steps. For
example, heterogeneous substrates have been successfully
fabricated by photolithography (McGall et al. JACS 1997
119:5081). However, photolithography is an expensive,
25   chemically intensive, and laborious process typically
requiring multiple steps to produce even a single pattern.
These steps include optical masking to selectively expose
and develop areas of photoresist material, followed by
etching or depositing material through the photoresist
30   masking pattern, and finally dissolving the photoresist
mask. Creating heterogeneous substrates by photolithography
requires repeating the alignment and registration steps for
each new pattern in order to ensure proper geometric

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relation between the patterns on the surface. Manual
alignment and registration of many different masks to the
substrate becomes increasingly difficult to control when the
critical feature size is micron or even sub-micron in

5   resolution or when the number of aligned patterns becomes
very large.   It is in these cases particularly, where the
ability to self-align the masking material onto the surface
is expected to be useful.

     Programmable assembly of micron-sized colloidal

10   particles, carrying various molecules, such as proteins, DNA
fragments or fluorescent labels, into precise geometric
patterns has been demonstrated using magnetic forces and
magnetically encoded surfaces (Yellen et al. J. Appl. Phys.
2003 93:7331). Previous work has shown that the number of

15   particles deposited (or not deposited) at each surface site
can be reliably controlled through a combination of magnetic
and morphological template features. Regular heterogeneous
colloidal patterns were assembled by this technique using
only physical forces (i.e. magnetic, hydrodynamic and

20   surface forces). The theoretical process of particle
assembly onto magnetic surfaces has also been analyzed in
order to guide experimental investigations (Yellen et al.
2002 J. Appl. Phys. 912:855; Yellen et al. J. Appl. Phys.
2003 93:8447; Plaks et al. IEEE Trans. Mag. 2003 39:1436;

25   and Hovorka et al. IEEE Trans Mag. 2003 39:2549).

     In the present invention, a method is provided for
depositing magnetic nanoparticles at programmed locations on
a substrate surface in order to mask selected sites rather
than to deliver molecules using magnetic particles as the

30   carriers. In this method, the magnetic nanoparticles are
programmed to accumulate at selected sites on the substrate
in order to mask these selected sites from, for example
ultraviolet radiation and/or chemically reactive molecules

or binding of a molecule such as a protein or a nucleic
acid.

Summary of the Invention

5   An object of the present invention is to provide
materials and methods for masking substrates using magnetic
nanoparticle masks. The method of the present invention
employs local magnetic field gradients, produced either by
magnets held external to or magnets embedded within a

10   substrate, to form a magnetic nanoparticle mask. Once
formed, the mask protects designated regions of the
underlying surface from modifying effects of ultraviolet or
other forms of radiation, from action of physical or
chemical etchants, from attachment of chemically reactive

15   molecules, from deposition of materials by evaporation,
sputtering or electrochemical processes, from ion
implantation, from diffusion of various small molecules or
particles and from any other substrate modifying processes.
       Another object of the present invention is to provide a

20   method for fabricating a multi-component pattern on a
substrate which comprises producing a first set of regions
of localized magnetic field maxima on a surface; applying a
suspension of magnetic nanoparticles to the substrate so
that the magnetic nanoparticles of the suspension aggregate

25   on top of the first set of regions of localized magnetic
field maxima, thereby masking the first set of selected
areas; exposing the substrate to a first modifying substance
to alter any unmasked sites of the substrate via exposure to
the first modifying substance; quenching or removing the

30   first modifying substance, if necessary; defining a second
set of regions of localized magnetic field maxima on the
substrate; applying magnetic nanoparticles to the substrate
so that the magnetic nanoparticles aggregate at the second

set of regions of localized magnetic field maxima, thereby
masking the second set of selected areas; exposing the
substrate to a second modifying substance to alter any
unmasked sites of the substrate via exposure to the second
5   modifying substance; and quenching or removing the second
modifying agent, if necessary. By repeating this procedure,
a series of different masking patterns can be used to build
up a heterogeneous multi-component pattern step by step.

10   **Brief Description of the Figures**
     Figures 1(a) through 1(d) are diagrams depicting
direction of attraction of ferrofluid in relation to the
external magnetic field bias. Figure 1(a) depicts ferrofluid
(black) attracted to the right-side of a ferromagnetic bit
15   (white rectangle with arrow denoting bit magnetization) by
external magnetic field bias applied perpendicularly to the
bit's magnetization. When the external field bias is
reversed, the ferrofluid is repelled from the right-hand
pole and attracted to the left-hand pole as illustrated in
20   Figure 1(b). Ferrofluid will deposit in between the bits
when external magnetic fields are applied parallel to the
bit's magnetization, as illustrated in Figure 1(c), and on
top of the bit when the applied field is reversed, as
illustrated in Figure 1(d).
25   Figures 2(a) and 2(b) are diagrams depicting how
ferrofluid accumulation can mask areas of photosensitive
film. Figure 2(a) depicts a photosensitive film on top of
the ferromagnetic alignment marks, and upon application of
external magnetic fields as shown in Figure 1(a), magnetic
30   nanoparticles accumulate on top of the photosensitive film,
thereby masking the photosensitive film from ultraviolet
exposure. Figure 2(b) depicts the photosensitive film after
exposure and development, leaving behind spots of

photosensitive resist where the magnetic nanoparticle mask had accumulated.

Figures 3(a) through 3(c) are diagrams depicting how ferrofluid accumulation can mask areas of a surface from 5 adsorption or reaction with chemically modifying reagents such as DNA fragments. Figure 3(a) depicts a set of bits that are masked by ferrofluid, while the other set of bits are not, thus allowing a solution containing DNA molecules with reactive complexes to chemically bond to the unmasked 10 locations. Figure 3(b) depicts the array after re-magnetization of the bits and exposure to a new solution containing DNA molecules with reactive complexes which modifies the new set of unmasked locations. Figure 3(c) depicts the heterogeneous chemical array after the two 15 masking steps.

Figures 4(a) through 4(f) is a sequence of images depicting the attraction of ferrofluid to one or the other end of a ferromagnetic bit by application of external magnetic fields as shown in Figures 1(a) and 1(b). The 20 attraction of the ferrofluid to one end is dependent on the magnetic fields applied. When the magnetic fields are reversed, the ferrofluid is repelled from the first end and attracted to the opposite end as shown in Figure 4(d) through 4(f).

25 Figures 5(a) through 5(d) are optical and SEM (Scanning Electron Microscope) images of positive Shipley 1813 photosensitive film patterns after masking, exposure to ultraviolet radiation and development.

Figures 6(a) through 6(f) are optical and SEM images of 30 negative NR-7 photosensitive film patterns after masking and exposure to ultraviolet radiation. Figures 6(a) and 6(b) are the masking patterns formed by magnetic fields applied to the substrate as shown in Figure 1(a), while Figures 6(d)

and 6(e) are the masking patterns formed by magnetic fields
applied to the substrate as shown in Figure 1(d). The
negative NR-7 photosensitive film is specifically formulated
for lift-off. After formation of the masking pattern in the
5 photoresist film, gold metal was evaporated on top of
substrate. Then the photoresist film was stripped,
resulting in a gold pattern aligned with respect to the
ferromagnetic bits.

10 **Detailed Description of the Invention**
     The present invention provides a soft masking method
that employs magnetic nanoparticle materials and the means
for arranging the magnetic nanoparticles on a surface using
regions of localized magnetic field maxima. External
15 magnets or magnets embedded inside a surface can be used to
generate regions of magnetic field maxima, which define and
automatically align sequences of magnetic nanoparticle
masking patterns. The magnetic nanoparticles can be
employed in a gas or liquid phase with a liquid suspension
20 of magnetic particles such as ultra-fine iron oxide grains
suspended in fluid (ferrofluid) being preferred. This
suspension can be programmed by external magnets to protect
and/or de-protect selected areas of a patterned substrate
according to a sequence. As shown herein, a suspension of
25 magnetic nanoparticles such as ferrofluid can be used to
assemble regular structures on patterned ferromagnetic film
or substrates, and controlled photoresist patterns can be
produced using the methodology of the present invention.
Further, the lithographic application of a suspension of
30 magnetic nanoparticles such as a ferrofluid in the present
invention is not limited to optical masking. These masking
techniques can also be applied as a diffusion mask during
solution-based synthesis. An advantage is that the mask

formation and material deposition can be combined into a
single step. For example, the accumulation of magnetic
nanoparticles on the magnetic pattern can be used to
restrict molecules, such as DNA or proteins, from assembling
5   at masked locations. Various techniques for molecular self-
assembly, including the gold-thiol (Pan et al. Langmuir 1996
12:4469) and SiO_2-siloxane (Xia et al. J. Am. Chem. Soc. 1996
117:9576) interactions, have been employed to create
molecular monolayers on a surface. The assembly of molecular
10   monolayers can be prevented by the magnetic nanoparticle
accumulation at these locations. The magnetic nanoparticle
diffusion masks can also be used to protect chemically
active regions of a surface from reaction with a component
that is introduced into the suspension. Another benefit is
15   that magnetic nanoparticle masks can be easily dissolved
without intensive chemical strippers. This gentle synthesis
approach of the present invention is expected to be useful
in patterning multiple layers of delicate biological
materials such as proteins and cells. However, these
20   masking techniques can also be used to protect and/or de-
protect a surface from alterations by other chemical or
physical etchants, various forms of radiation, by ion
implantation, by neutron beam exposure, or by any substrate
modifying process.
25   In this method, nanometer sized magnetic particles,
referred to herein as nanoparticles, are applied to a
substrate in suspension and deposited at programmed
locations on a surface of ferromagnetic bits. The magnetic
nanoparticles can range from single molecules to particles
30   with diameters of hundreds of nanometers, more preferably
from 5 to about 20 nanometers. Magnetic nanoparticles may
comprise iron oxide, cobalt, nickel, iron, iron platinum,
rare earth materials, paramagnetic ions, molecular magnets,

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and any superparamagnetic or weakly ferromagnetic material
that is suspended in gas or in various solvents, such as
water, alcohol, or organic based-solvents. An exemplary
suspension of magnetic nanoparticles useful in the present
5   invention is a ferrofluid which comprises a liquid
suspension of ultra fine iron oxide particles. Magnetic
nanoparticle suspensions such as ferrofluid provide a
desirable alternative to micron-sized and sub-micron sized
polymerized beads loaded with magnetic grains (such as those
10   produced by Dynal Biotech or Spherotech) because the
diffusion coefficient of sub 20-nm particles is large.
Also, magnetic nanoparticle solutions such as ferrofluid do
not settle out in solution as micron-sized particles are
prone to do. Since the masking resolution is ultimately
15   limited by the magnetic nanoparticle size, smaller magnetic
nanoparticles are usually preferred.

In contrast to prior art methods such as taught in WO
01/51668 wherein the goal is to deliver molecules to a
particular site, the goal in the present invention is to
20   mask particular locations of the surface from exposure to
ultraviolet radiation, chemically reactive molecules,
binding of a molecule such as a protein or nucleic acid,
chemical or physical etchants, ion implantation, or neutron
or electron beam exposure. The magnetic nanoparticle mask is
25   self-formed by application of external magnets held near or
embedded directly inside the substrate. External magnetic
pins, for example, can be held directly underneath the
substrate. These pins create strong local magnetic field
maxima for attracting the magnetic nanoparticles. Magnetic
30   film can also be embedded inside or patterned directly on
top of the substrate. For this application, a ferromagnetic
film is preferred because it can retain memory and can be
remotely programmed by existing magnetic recording methods.

Thus, the masking technique allows for self-aligned programmable mask formation by recoding specific states in the magnetic film elements.

A diagram of the general process of field-assisted
5   magnetic nanoparticle suspension assembly onto a recordable magnetically patterned substrate in accordance with the present invention is shown in Figure 1(a) through 1(d). In this process, a recordable magnetically patterned substrate is subjected to a uniform external magnetic field applied
10   perpendicularly to the magnetization of the patterned substrate. The uniform external magnetic field magnetizes the nanoparticles of the suspension and preferentially draws the nanoparticles to one of the poles of the magnetic pattern of the substrate. The nanoparticles can be switched
15   to the opposite pole by simply reversing the external magnetic field bias. Thus, depending on the external field orientation and hence particle magnetization, nanoparticles of the suspension will be preferentially deposited at specific locations with respect to the bits of the
20   recordable magnetic pattern. For example, as shown in Figure 1(a) and 1(b), when the external field is applied normal to the plane, nanoparticles accumulate over one or the other pole. Alternatively, as shown in Figure 1(c) and 1(d), when the external field is applied in the plane with
25   orientation parallel or anti-parallel to the substrate magnetization, the nanoparticles assemble in between or on top of the substrate. Preferential deposition is used to selectively mask certain locations on the surface from exposure to ultraviolet radiation, physical or chemical
30   etchants, or chemicals or binding of a molecule.

Diagrams of ferrofluid masking against ultraviolet exposure and chemically reactive molecules are shown in Figures 2 and 3. Figures 2(a) and 2(b) are diagrams

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depicting how ferrofluid accumulation can mask areas of
photosensitive film. Figure 2(a) depicts a photosensitive
film on top of the ferromagnetic bits, and upon application
of external magnetic fields like that shown in Figure 1(a),

5   magnetic nanoparticles accumulate on top of the
photosensitive film, thereby masking the photosensitive film
from ultraviolet exposure. Figure 2(b) depicts the
photosensitive film after exposure and development, leaving
behind spots of photosensitive film where the magnetic

10   nanoparticles had accumulated.

      Figures 3(a) through 3(c) are diagrams depicting how
ferrofluid accumulation can mask areas of a surface from
adsorption or reaction with chemically modifying reagents
such as DNA fragments. Figure 3(a) depicts a set of magnetic

15   bits that are masked by ferrofluid, while the other set of
magnetic bits are not, thus allowing a solution of DNA to
modify the unmasked locations. Figure 3(b) depicts the array
after re-magnetization of the bits and exposure to a new
solution of DNA which modifies the new set of unmasked

20   locations. Figure 3(c) depicts the heterogeneous chemical
array after the two masking steps.

      Results from experiments wherein ferrofluid masks were
used in accordance with the present invention are shown in
Figures 4, 5 and 6. Figures 4(a) through 4(f) show a

25   sequence of images depicting the attraction of ferrofluid to
one or the other end of a magnetic bit by application of
external magnetic fields as shown in Figures 1(a) and 1(b).
The attraction of the ferrofluid to one end is dependent on
the magnetic fields applied. When the magnetic fields are

30   reversed, the ferrofluid is repelled from the first end and
attracted to the opposite end as shown in Figure 4 (d)
through 4(f).

Figures 5(a) through 5(d) are optical and SEM images of positive Shipley 1813 photosensitive film patterns after masking and exposure to ultraviolet radiation.

Figures 6(a) through 6(f) are optical and SEM images of
5   negative NR-7 photosensitive film patterns after masking and exposure to ultraviolet radiation. Figures 6(a) and 6(b) are the masking patterns formed by magnetic fields applied to the substrate as shown in Figure 1(a), while Figures 6(d) and 6(e) are the masking patterns formed by magnetic fields
10 applied to the substrate as shown in Figure 1(d). The negative NR-7 photosensitive film is specifically formulated for lift-off. After evaporation of gold metal on top of the photosensitive patterned film and then stripping of the photosensitive film, a gold pattern is formed aligned with
15 respect to the magnetic bits. See Figures 6(c) and 6(f).

Fabricating multi-component patterns using a suspension of magnetic nanoparticles in accordance with the present invention relies on the ability to record the magnetization of selected areas of the recordable magnetic
20 substrate in an "on" or "off" state. One method for creating the "on" and "off" sites is to place a set of magnetic pins near chosen sites of a surface. The positions closest to the pins are the regions of magnetic field maxima, corresponding to the "on" state. In the "on" state,
25 the presence of magnetic nanoparticles prevents exposure of the substrate to ultraviolet radiation, or chemicals, or binding of a molecule to the substrate to take place, while in other areas of the substrate in the "off" state, the absence of the magnetic nanoparticle coating allows such
30 exposure or binding or any substrate modifying process to take place. In another method, the "on" and "off" sites are produced by materials embedded in the surface. These materials can be designed with ferromagnetic properties

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containing bistable states that can be programmed by
existing thermomagnetic recording methods. Here,
application of an external uniform magnetic field can
promote some regions of the ferromagnetic material to
5   contain the magnetic field maxima, and other regions of the
material to contain the magnetic field minima. The mask
will accumulate on the magnetic field maxima, corresponding
to the "on" state, while avoiding the magnetic field minima,
corresponding to the "off" state. The regions of magnetic
10 field minima and maxima can be shifted by re-programming the
ferromagnetic material in a different direction. The re-
programming process of addressable ferromagnetic bits can be
accomplished using thermomagnetic recording methods, wherein
low strength magnetizing fields are applied across large
15 portions of the substrate while a focused laser beam heats
selected areas. The increase in temperature reduces the
coercive switching fields of heated portions versus unheated
portions of the substrate, thus allowing only the
ferromagnetic bits in the heated portions of the substrate
20 to have their magnetization switched in the presence of the
magnetizing fields.

A heterogeneous pattern of multiple components can be
created using a series of steps wherein a first set of
regions of a substrate is turned on to allow accumulation of
25 a magnetic nanoparticle mask. A physical or chemical etchant
or chemical reagent or reagents, or ultraviolet radiation or
another form of radiation, or electron, ion or neutron beam,
or other surface modifying process is introduced into the
system in order to modify the unmasked sites. Some examples
30 of chemically reactive agents are DNA fragments and proteins
that react with surface groups through covalent or ionic
interactions. This is followed by quenching of the reaction
and rinsing of the excess reagent, if necessary. Additional

examples of modifying substances include, but are not
limited to, electrochemical reactions intended to deposit or
remove material to or from the unmasked regions of the
substrate, deposition or removal of material by evaporation,
5   and deposition or removal of material by ion beam, electron
beam, neutron beam or other similar means to or from
unmasked regions of the substrate.   The surface is then re-
programmed to accept different surface modifications at
newly recorded locations. For applications employing
10 magnets embedded in this substrate, this re-magnetizing of
the surface includes turning off select areas that were
turned on in the previous step, as well as turning on a new
set of select areas to be modified in the next step. By
repeating this procedure for each type of component, a
15 heterogeneous pattern can be built up step by step in a
complete, self-aligned manner.

        After masking, the magnetic nanoparticles can be re-
suspended by simply reversing or removing the applied
magnetic field bias. The magnetic nanoparticles can also be
20 easily washed away. Spatial programming of the mask in each
step can be accomplished by recording the magnetization
direction of the individual magnetic bits, and thus the
positions of the desired locations to be masked.

        Patterning by magnetic nanoparticle masking in
25 accordance with the present invention provides significant
advantages over other masking techniques. For example, one
advantage is that magnetic nanoparticles of the suspension
automatically align with the regions of magnetic field
maxima on the substrate surface. When the external magnets
30 are embedded directly in the substrate, an inherent self-
alignment feature eliminates the need for manual alignment
of the mask after each step, as is required in
photolithographic patterning. Using a recordable magnetic

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pattern and selected areas thereof, resolution of 50 nm or
better is expected. Traditional photolithographic
techniques, by contrast, have difficulty in aligning
multiple patterns with micrometer resolution. Another

5   advantage is that the suspension of magnetic nanoparticles
has been shown to perform consistent masking even through
barriers of micrometer thickness. The accumulation of
magnetic nanoparticle masks at long range indicates that
masking can also be accomplished with magnetic bits that are

10 embedded substantially inside the substrate or even held
externally to a thin substrate. Embedded magnetic bits allow
patterning to be performed on a surface that has uniform
surface chemistry, which is essential for applications in
combinatorial chemistry, genomic analysis, and drug

15 discovery. In addition, the magnetic nanoparticle mask can
be dissolved by simply turning off or reversing the external
magnetic field bias. Therefore, no harmful chemical solvents
need to be employed to remove the masking layer. Thus, the
magnetic nanoparticle liquid masks are far more convenient

20 than photolithographic patterning techniques which use a
solid photoresist mask that has to be dissolved with harsh
chemical solvents after each step. Accordingly, magnetic
nanoparticle masks provide a fast, inexpensive, and gentle
route to creating heterogeneous nanopatterns.

25   The method of the present invention can be used in
various lithographic applications including, but not limited
to, optical masking, diffusion masking, physical or chemical
etch masking, masking against sputtering or evaporation of
material onto a surface, and masking against electron,

30 neutron or ion beam implantation. This fabrication method is
especially suited to applications in genomic analysis, cell
patterning, and drug discovery, where many different
molecules (often greater than 100 types of molecules) need

to be patterned on a surface with high resolution. The
advantage of self-aligned patterning is demonstrated more
clearly as the number of components in the pattern
increases. In addition, magnetic nanoparticle masks are
5   uniquely capable of assembling heterogeneous biological
systems, as many different biological materials can be
assembled inside magnetic nanoparticle fluids without
altering, damaging or destroying previously deposited
materials with the harsh chemicals used in traditional
10   masking techniques.

The efficacy of this masking was demonstrated using
Cobalt films. Recordable magnetic patterns were made in
evaporated Cobalt film 100-nm in thickness by conventional
photolithographic lift-off methods. The magnetic patterns
15   used in these experiments were 4-microns wide and 20-microns
long. Following patterning, the substrate was submersed in a
bath of deionized water and an aqueous solution of domain-
detection ferrofluid (purchased from Ferrotec, Inc., NH,
USA) was injected into the bath under the influence of
20   applied magnetic fields.

The programmability of this process was demonstrated by
alternating the magnetic field bias, thereby causing the
ferrofluid that accumulated at one pole to switch to the
opposite pole in a matter of seconds. Images taken from
25   video footage confirm this switching behavior of ferrofluid
in the presence of an oscillating external magnetic field
bias. In these experiments, the ferrofluid initially coated
the left end of the magnetic bits, because of external
magnetic fields that bias the ferrofluid to be attracted to
30   one pole. However, the ferrofluid switched to the opposite
pole when the magnetic field bias was reversed. Previously
restricted locations were unmasked so that molecular
monolayers are permitted to assemble at or chemicals are

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permitted to react with those unmasked locations. Complete
switching of the ferrofluid from one side to the other was
accomplished in under a few seconds. This switching
phenomenon can thus be used to create heterogeneous
5   molecular patterns. Further, various patterns can formed on
the substrate depending upon the field orientation. The
thickness of the ferrofluid layer, measured by AFM, was
observed to be micrometers thick in certain locations.

The ability of ferrofluid to act as an optical mask was
10   demonstrated using positive Shipley 1813 photoresist and
negative NR-7 photoresist spun onto a wafer containing a
pattern of Cobalt magnetic bits. A drop of ferrofluid was
dispensed onto the wafer and a cover glass slide was placed
on top of the ferrofluid in order to promote the formation
15   of an optically transparent ferrofluid film. When external
magnetic fields were applied, the ferrofluid accumulated
over one pole of the magnetic bit while avoiding the other
pole. The optical contrast between the two poles was used as
a photolithographic mask against flood exposure by
20   ultraviolet radiation. In particular, the wafer with
ferrofluid mask was exposed to I-line ultraviolet radiation
(365nm). In these experiments, the bake times, spin speeds,
and other processing parameters were kept constant. Masking
conditions were varied by adjusting the ferrofluid
25   concentration and ultraviolet exposure time.

SEM analysis of a typical photoresist spot over the
poles averaged approximately 8-pm in diameter with great
uniformity among spots across the wafer. The slope of the
photoresist side-walls was approximately 45° as measured by
30   AFM.

In addition to the above experiments, the process of
ferrofluid assembly onto magnetized film has also been
studied theoretically to determine if ferrofluid can form a

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stable blockage and prevent the diffusion of other molecules onto the surface of the magnetic bit.

In stabilized magnetic colloids, where spontaneous magnetization does not occur in the absence of a magnetic field, equilibrium regions of particle aggregation are the result of competition between diffusion and magnetic forces. In many previous models in the literature, magnetic forces on particles were calculated using the assumption that the non-magnetic carrier fluid is incapable of screening external magnetic fields. This assumption is valid only in the regions of relatively low particle concentrations. Moreover, previous models of high gradient magnetic separation schemes (HGMS) ignored possible perturbation of the external magnetic fields by the spatially varying concentrations of the magnetic particles in the fluid. Volume susceptibility of the fluid at higher magnetic particle concentrations can be as high as 10. Thus, neglecting the demagnetizing field due to the spatially varying concentration is justified only at lower concentrations far away from any magnetic wires or magnetic poles placed in the fluid. The self-consistent model presented below takes into account both the magnetic field screening by the fluid and the demagnetizing field due to spatially varying particle concentration.

Volume magnetization, M_p, of a particle is dependent on external magnetic field H (which is assumed to be uniform inside the particle). For relatively weak magnetic fields, the relationship between the magnetization and magnetic field is linear and in the vector form can be written as follows:

$$\vec{M}_p = \chi \vec{H}, \vec{m}_p = V_p \vec{M}_p, \chi = \frac{\mu_0 V_p M_s^2}{3 k_B T} \qquad (1)$$

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where m_p is the magnetic moment of a particle of volume,
V_p, M_s is saturation magnetization of particles, k_B is
Boltzmann constant, and T is the absolute temperature.

The force acting on a particle inside magnetic fluid
takes the form:

$$\vec{F}_m = \mu_0 (\vec{m}_p - \langle \vec{m} \rangle) \cdot \nabla \vec{H} \qquad (2)$$

where $\langle \vec{m} \rangle$ represents an average magnetic moment of unit
volume of magnetic fluid surrounding the particle. It is
assumed that $\langle \vec{m} \rangle$ at a given point in space is related to m_p
by:

$$\langle \vec{m} \rangle = \vec{m}_p C(\vec{r}) \qquad (3)$$

where $C(\vec{r})$ is the volume concentration of particles
(fraction of volume occupied by the particle material). The
balance of force $\vec{F}_m$ on the magnetic particle and the fluid
drag determines the velocity of the particle (Stoke's law)

$$\vec{v}_p = \eta \vec{F}_m = \eta \mu_0 (\vec{m}_p - \langle \vec{m} \rangle) \cdot \nabla \vec{H} \qquad (4)$$

where the coefficient of proportionality η is the
mobility of the particle, which characterizes the fluid
drag. The effects of magnetic field screening due to the
fluid magnetization are taken into account in (2) and (4) by
subtracting the average fluid magnetization. This is one of
the main differences with respect to previous models
employed in HGMS.

The total flux of particles is the sum of two
components, a diffusion component

$$\vec{J}_{diff} = -D \nabla C(\vec{r}) \qquad (5)$$

and a drift component

$$\vec{J}_{drift} = C(\vec{r}) \vec{v}_p \qquad (6)$$

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Under static equilibrium conditions the total flux of particles must be zero,

$$\vec{J} = \vec{J}_{diff} + \vec{J}_{drift} = 0. \qquad (7)$$

Using (3-7) one obtains

$$\nabla C(\vec{r}) = (k_B T)^{-1} C(\vec{r})(1 - C(\vec{r}))\mu_0 \bar{m}_p \cdot \nabla \vec{H} \qquad (8)$$

where, from the Einstein relation, $(k_B T)^{-1} = \eta/D$, and C is the unknown concentration of magnetic particles.
Substituting m_p defined in (1), equation (8) can be directly re-arranged as follows:

$$\frac{\nabla C(\vec{r})}{C(\vec{r})(1 - C(\vec{r}))} = \nabla \ln \frac{C}{1 - C} = \nabla \frac{\mu_0 \chi V_p H^2}{2 k_B T} \qquad (9a)$$

Given that the bulk of the fluid is in zero field (far away from any field sources) and has bulk particle concentration C_i, equation 9(a) can be integrated to yield:

$$\frac{C(\vec{r})}{(1 - C(\vec{r}))} = \frac{C_i}{(1 - C_i)} \exp\left(\frac{\mu_0 \chi V_p H^2}{2 k_B T}\right) = A \exp\left(\frac{\alpha^2}{6}\right) \quad (9b)$$

wherein the constant A and function $\alpha(\vec{r}) = \frac{\mu_0 V_p M_s}{k_B T} H(\vec{r})$, are dimensionless quantities defined for the sake of convenience. Expression for concentration can be obtained from (9b) by simple algebraic manipulation:

$$C(\vec{r}) = \frac{1}{1 + A^{-1} \exp(-\alpha^2/6)}, \qquad (10)$$

It is important to note that the dimensionless function α can be interpreted as the ratio of two energies: particle's potential energy in the external magnetic field and its thermal fluctuation energy. From this, it is clear that spatial variation of concentration in (10) is completely consistent with equilibrium statistical mechanics. In fact, the right hand side of (10) can be recognized as the Fermi-Dirac function. It emerges as a result of field screening by magnetic particles in the

solution, which reduces the magnetic force to zero at 100%
concentration. In the presence of diffusion this does not
allow particles to overlap. The impossibility of particle
overlap leads to Fermi-Dirac distribution in much the same

5   way as it happens due to the exclusion principle in quantum
mechanics. Therefore, concentration saturation emerges
naturally in this model without the need to use artificially
set hard concentration limits often imposed in HGMS models
that do not take field screening into account.

10   In determining average magnetization of the fluid,
effects of particle interactions were neglected above. Mean
spherical model takes into account interactions between the
particles by introducing a correction to the noninteracting
particle model discussed above, which can be written in the

15 linear regime of weak magnetic field as:

$$\langle \vec{m} \rangle = (1 + aC(\vec{r}))C(\vec{r})\vec{m}_p = (1 + aC(\vec{r}))C(\vec{r})V_p\chi\vec{H} \qquad (11)$$

where χ is zero-field susceptibility defined through (1),
and parameter a typically has a value around 3, making the

20 effects of concentration important when the concentration is
greater than roughly 20-30%.

Using equation (4-7) and (11) and following the line of
reasoning used to derive (9a), the following is derived:

$$\frac{\nabla C}{C(1-C)(1+aC)} = \nabla\left(\frac{\mu_0 V_p \chi H^2}{2k_B T}\right) = \nabla\frac{\alpha^2}{6} \qquad (12)$$

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Just like (9a), the above equation can be integrated to
yield:

$$\frac{C(\vec{r})}{(1-C(\vec{r}))^{1/1+a}(1+aC(\vec{r}))^{a/1+a}} = A_{MS}\exp\left(\frac{\mu_0 V_p \chi H^2}{2k_B T}\right) = A_{MS}\exp(\alpha^2/6) \qquad (13)$$

where the function α is defined as in (9b) and

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$$A_{MS} = \frac{C_i}{(1-C_i)^{1/1+a}(1+aC_1)^{a/1+a}}$$ is the integration constant

evaluated as before by setting the field equal to zero and
using the bulk fluid value of the concentration C_i.

The following nonlimiting example is provided to
5   further illustrate the present invention.

EXAMPLES

Example 1: Materials and Methods

Experiments were performed using Silicon or Pyrex
10   substrates patterned with 100 nm thick Cobalt bits by
conventional photolithographic lift-off process. In the
lift-off process, an image is defined by exposing
photoresist to ultraviolet radiation through a patterned
optical mask. The photoresist pattern is developed, and then
15   Cobalt is evaporated onto the patterned wafer. Finally, the
remaining photoresist is stripped to produce a pattern of
Cobalt film. While negative or multi-layer resists are
frequently utilized to obtain an undercut resist profile,
positive Shipley 1813 photoresist yielded satisfactory
20   results. Individual bits in these experiments have a planar
dimension of 4 pm by 20 pm. Aqueous based ferrofluid domain
detection fluid purchased from Ferrotec was applied to the
substrate in varying concentrations to determine optimal
masking conditions. The resulting ferrofluid masks were
25   observed in a fluidic bath using a Leica DM LFS microscope
with fluid-immersion lens. Ferrofluid masks were also
observed as a thin coating of the substrate formed by
placing a cover glass slide on top of a drop of ferrofluid.

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